



Calcium and Oxygen Isotopic Composition of Calcium Carbonates

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Different isotopic systems are influenced in multiple ways corresponding to the crystal structure, dehydration, deprotonation, adsorption, desorption, isotope exchange and diffusion processes.

In this study we investigated the structural and kinetic effects on fractionation of stable Ca- and O-isotopes during CaCO_3 precipitation. Calcite, aragonite and vaterite were precipitated using the CO_2 diffusion technique^[1] at a constant pH of 8.3, but various temperatures (6, 10, 25 and 40°C) and precipitation rates R ($10^{1.5}$ to $10^5 \mu\text{mol h}^{-1} \text{m}^{-2}$).

The calcium isotopic fractionation between solution and vaterite is lower ($\Delta^{44/40}\text{Ca} = -0.10$ to -0.55‰) compared to calcite (-0.69 to -2.04‰) and aragonite (-0.91 to -1.55‰). In contrast the fractionation of oxygen isotopes is highest for vaterite (32.1‰), followed by aragonite (29.2‰) and calcite (27.6‰) at 25°C and equilibrium. The enrichment of ^{18}O vs. ^{16}O in all polymorphs decreases with increasing precipitation rate by around -0.7‰ per $\log(R)$. The calcium isotopic fractionation between calcite/ vaterite and aqueous Ca^{2+} increases with increasing precipitation rate by $\sim 0.45 \text{‰}$ per $\log(R)$ and $\sim 0.1 \text{‰}$ per $\log(R)$ at 25°C and 40°C, respectively. In contrast the fractionation of Ca-isotopes between aragonite and aqueous Ca^{2+} decreases with increasing precipitation rates.

The large enrichment of ^{18}O vs. ^{16}O isotopes in carbonates is related to the strong bond of oxygen to the small and highly charged C^{4+} -ion. In contrast equilibrium isotopic fractionation between solution and calcite or vaterite is nearly zero as the Ca–O bond length is similar for calcite, vaterite and the hydrated Ca. Aragonite incorporates preferentially the lighter ^{40}Ca isotope as it has very large Ca–O bonds in comparison to the hydrated Ca. At the crystal surface the lighter ^{40}Ca isotopes are preferentially incorporated as dehydration and diffusion of lighter isotopes are faster. Consequently, the surface becomes enriched in ^{40}Ca . On the other hand, ^{40}Ca may desorb more easily, especially if the bond strength is lower as in the case of aragonite. For kinetic oxygen isotopic fractionation, the faster deprotonation of $\text{HC}^{16}\text{O}_3^-$ and the faster incorporation of $\text{C}^{16}\text{O}_3^{2-}$ at the surfaces causes a smaller enrichment of ^{18}O in all three polymorphs, which will be preserved at higher precipitation rates.

In consequence to the different behavior of calcium and oxygen isotopes, they can be useful for multiproxy applications. Thereby calcium isotopes can be used to identify kinetic effects, especially if both aragonite and calcite, can be analyzed in one sample. Oxygen isotopes are more strongly related to temperature.

^[1]A. Niedermayr, S.J. Köhler and M. Dietzel (2013), *Chemical Geology*, 340, 105-120.